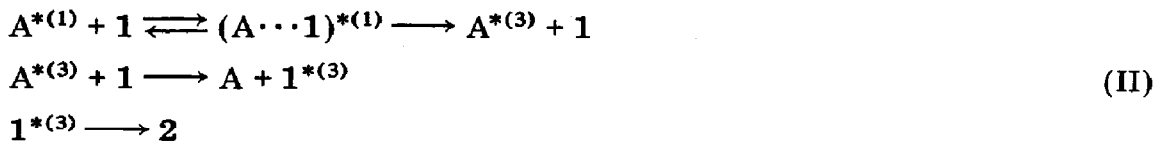




A kinetic analysis revealed that the alternative mechanism



involving exciplex-mediated intersystem crossing and triplet sensitization could produce kinetic results (an approximately linear plot of $1/\Phi$ versus $1/[1]$) indistinguishable from those expected for mechanism (I) provided that energy transfer from $A^{*(3)}$ to 1 occurs faster than diffusion from the solvent cage in which the $A^{*(3)}$ -1 pair is formed [10, 11]. (Triplet sensitization of 1 appears to occur before the sensitizer triplets formed by quenching can diffuse from 1, consistent with the requirements of mechanism (II), when 1 quenches phenanthrene or triphenylene singlets in acetonitrile [12].) As we have noted, distinguishing between these two mechanisms in exciplex-mediated reactions may be difficult unless sufficient rate constant data are available to eliminate mechanism (II) or unless it can be demonstrated that $A^{*(3)}$ does not sensitize the photoreaction [10, 11]. If unimolecular intersystem crossing of $A^{*(1)}$ to $A^{*(3)}$ is slow, then the results of the $A^{*(3)}$ sensitization of 1 may not be known. In this communication we report the results of applying heavy atom techniques to the problem of distinguishing between the two mechanisms for the 2-methoxynaphthalene-sensitized isomerization of 1 to 2.

2. Experimental details

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM 360-L NMR spectrometer; the solvent was $CDCl_3$ containing 5% tetramethylsilane. Gas chromatographs were obtained using a Hewlett-Packard 5710A gas chromatograph with flame ionization detection. The column was 6 ft long by 1/8 in wide and contained 10% SE-30 on Chromosorb G-HP; the column temperature was programmed from 130 to 200 °C at 8 °C min^{-1} during the analysis. IR spectra were obtained using a Perkin-Elmer model 700 IR spectrophotometer. The fluorescence spectra were obtained using a Perkin-Elmer 650-40 fluorescence spectrophotometer.

2.1. Synthesis of dimethyl norbornadiene-2,3-dicarboxylate

Freshly cracked cyclopentadiene (33.1 g (0.5 mol) from technical Eastman dicyclopentadiene) was added dropwise to freshly distilled dimethylacetylenedicarboxylate (89.2 g (0.63 mol), Eastman) in a cooled 250 ml round-bottomed flask. After completion of the reaction the product was fractionally distilled three times. The final yield of product was 67 g (64%) of 1 boiling from 85 to 86 °C at 0.15 Torr (published value, 134 - 135 °C at

10 - 11 Torr [13]). The NMR data were as follows: $\delta = 6.78$ ppm, triplet (2H); $\delta = 3.84$ ppm, singlet (2H); $\delta = 3.72$ ppm, singlet (6H); $\delta = 2.14$ ppm, multiplet (2H). The IR spectrum was as follows: 3000, 2950, 2870, 1620 and 1710 (broad) cm^{-1} .

2.2. Purification of other compounds

2-methoxynaphthalene (Eastman) was recrystallized from absolute ethanol and sublimed. Bromobenzene (B&A, reagent grade) was eluted through activated alumina and distilled under nitrogen from anhydrous K_2CO_3 . A center cut was taken at 154 °C. Durene (Eastman) and cyclohexane (MC&B, spectroquality) were used as received.

2.3. Preparation of samples

Pyrex test tubes (13 mm \times 100 mm) were cleaned with KOH-alcohol solution and matched for fluorescence using the same concentration of 2-methoxynaphthalene in cyclohexane employed for further experiments. A matched set of tubes was recleaned and constricted. Cyclohexane solutions were prepared containing 2-methoxynaphthalene (9.4×10^{-5} M), **1** (8.6×10^{-4} M), bromobenzene concentrations ranging from 0 to 0.12 M and durene as an internal standard. Aliquots (3.0 ml) of each solution were degassed by several freeze-pump-thaw cycles and sealed at pressures less than 10^{-2} Torr. The relative intensities of the 2-methoxynaphthalene fluorescence (345 nm) were measured. The samples were irradiated to less than 5% conversion with Pyrex-filtered light from a 450 W mercury lamp in a carousel apparatus [14] and relative yields of **2** were determined by gas chromatography.

3. Results and discussion

The relative intensities F and F' of 2-methoxynaphthalene fluorescence with and without bromobenzene were determined. The relative quantum yields Φ and Φ' of appearance of **2** were also determined for samples with and without bromobenzene. Under our conditions 2-methoxynaphthalene absorbed essentially all the light. With the concentrations used here, some product formation resulting from the quenching of $\text{A}^{*(1)}$ by **1** occurs but it is accounted for in the kinetic analysis [11]. Figure 1 shows a plot of $(F'/F)(\Phi/\Phi')$ versus $[\phi\text{-Br}]$. The plot is linear (correlation greater than 0.99) with slope 11 M^{-1} , confirming that triplets of 2-methoxynaphthalene can sensitize the $1 \rightarrow 2$ isomerization [10, 11]. (Our results indicate that unimolecular intersystem crossing of 2-methoxynaphthalene and subsequent triplet sensitization of **1** to **2** could be a competing pathway for product formation when the concentration of **1** is low enough that some 2-methoxynaphthalene singlets are not quenched, regardless of whether the singlet-sensitized product arises via mechanism (I) or mechanism (II). (For a detailed kinetic analysis, see the discussion of case II in ref. 11.) The present discussion concerns only the multiplicity of the reaction pathway following singlet quenching events.) Since triplet formation has been observed in the quenching of 2-methoxynaphthalene singlets by chloroacetonitrile in a polar

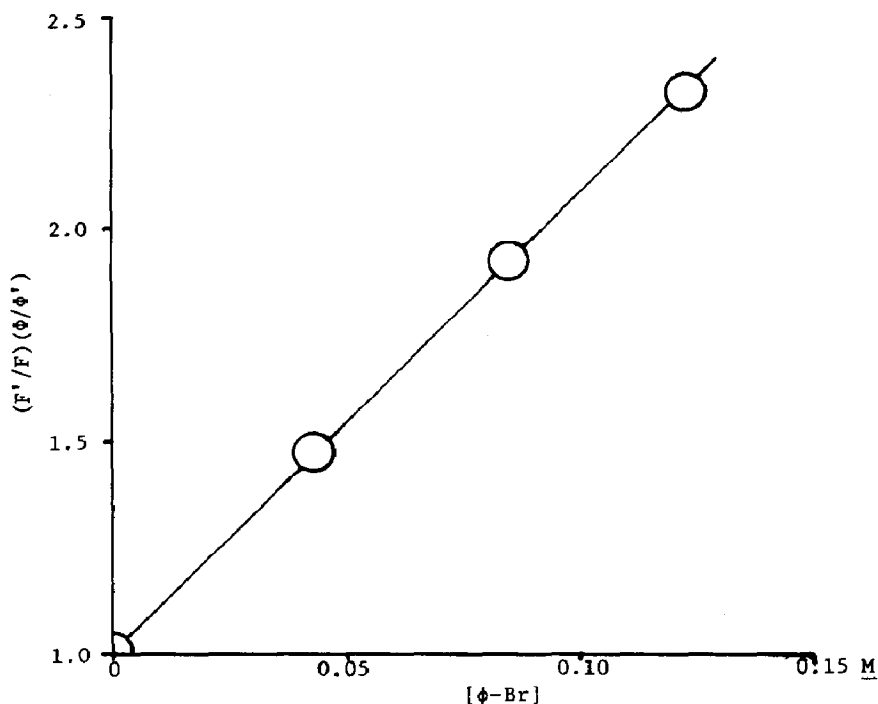


Fig. 1. Plot of $(F'/F)(\Phi/\Phi')$ vs. $[\phi\text{-Br}]$.

solvent [15], there is some precedent for the view that triplets may also be formed by quenching with 1 in cyclohexane. Although a more complete understanding of the role that the solvent plays in exciplex decay processes will be necessary before firm conclusions can be drawn, mechanism (II) would seem to offer a reasonable explanation for the formation of 2 upon quenching of 2-methoxynaphthalene singlets by 1 in cyclohexane. (For a discussion of solvent effects in the sensitized isomerization of 2 to 1 see ref. 16.)

It is likely that mechanism (II) as presented above understates the complexity of the reaction process. Intersystem crossing of the singlet exciplex to a triplet exciplex may be involved as an intermediate step [17] and either $A^{*(3)}$ or $1^{*(3)}$ could be the initial result of exciplex dissociation. Spectroscopic or chemical detection of $A^{*(3)}$ formed from quenching would provide evidence for the formation of discrete sensitizer triplet states, but such detection is unlikely as long as the quencher is a good triplet energy acceptor. However, the quantum yield profile for the photoisomerization of 1 to 2 sensitized by aromatic singlets has been reported to follow the triplet energy profile of the sensitizers in non-polar solvents and to decrease rapidly for sensitizers with triplet energies less than that of 1 [18]. (A referee has noted that the failure of methoxyanthracenes to sensitize the isomerization of 1 to 2 [5] may also be a function of their low triplet energies.) These results seem more consistent with processes involving $A^{*(3)}$ as a discrete intermediate. If triplets of $1^{*(3)}$ are formed directly from an exciplex, it might

be expected that some of the excitation energy of the sensitizer would remain to help to drive the triplet reaction.

The heavy atom technique has been exploited previously by a number of groups for elucidating photochemical and photophysical processes. A constant potential complication of such studies is that heavy atom additives may be incorporated into molecules that can quench with multiple decay pathways, including charge transfer interactions, which may or may not lead to triplet states [19]. However, xenon has been shown to quench singlets to triplets efficiently [20], and there is no evidence that processes other than singlet-to-triplet conversion are important with bromobenzene. We note that mechanism (II) retains one attractive feature of mechanism (I): because product formation occurs directly as a result of singlet quenching, the reaction may be less sensitive to oxygen or other triplet quenchers than would be the case with classical triplet sensitization processes. Thus exciplex-mediated intersystem crossing may be an attractive alternative mechanism for solar energy capture systems involving triplet-sensitized reactions.

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